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X-Ray Analysis in Industry

The Institute of Physics has performed a very useful function recently in inviting contributions of papers dealing with the methods and applications of X-ray analysis from research workers in university and industrial laboratories. These papers are published in the May and July numbers of the *Journal of Scientific Instruments*, and although they range over many branches of chemistry, metallurgy and mineralogy, there are a number which will be of general interest to metallurgists who are not experts in the specialised study of crystal structure.

Applications of X-ray methods to the investigation of the constitution of alloys, to the measurement of internal stress, to the determination of crystal size and orientation and to the sub-microscopic structures within each individual crystal, such as occur in age hardening and other types of imperfect phase precipitation, all receive attention. As indicated in papers by Dr. A. H. Jay and Mr. H. P. Rooksby, X-ray methods have proved to be invaluable in solving metallurgical problems associated with refractories. Such methods have also been used to identify the nature of the non-metallic inclusions in steels which have been deoxidised by various additions to the molten metal.

One very interesting paper by H. J. Goldschmidt and G. T. Harris draws attention to a new approach to the problem of mechanical wear or abrasion under non-lubricated conditions in air. The fine powders produced by dry abrasion of iron and steels were collected and subjected to X-ray analysis. Highly diffused diffraction lines were first shown by the powders collected, but after these had been annealed *in vacuo* at a moderate temperature sharp lines were obtained. From data obtained on a range of carbon steel samples the following conclusions were drawn :—

(1) The wear powder consists of iron oxides and some of the parent metal (ferrite); (2) the observed oxides are magnetite Fe_3O_4 and woosite FeO; (3) the relative amounts of Fe, FeO and Fe_3O_4 depend on the composition and constitution of the steel and on other relevant factors, such as pressure; (4) hæmatite, Fe_2O_3, the oxide richest in oxygen, is never found; (5) cementite, Fe_3C, occurs in some of the powders from the higher carbon steels and its presence is accompanied by an increase in FeO content; (6) the heating and cooling effect of wear can be considered as equivalent to a kind of localised heat treatment both on the powder and on the material.

The absence of Fe_2O_3 from all of the wear powders was a striking feature in view of its common occurrence as a result of ordinary oxidation. It has been shown, however, that the crystal structures of α-Fe, FeO and Fe_3O_4 (all cubic) bear certain very simple relations to one another and that they can be readily transformed from one to another while considerably greater energy is needed to produce the Fe_2O_3 structure. In view of the very small time and the limited supply of oxygen available for chemical reaction during natural wear, the absence of Fe_2O_3 can be explained. It would appear that the X-ray method could with advantage be employed in the study of the fundamentals of the wear process in other metals and alloys.

It would be possible to select other interesting examples of information conveyed by these papers, but the whole series is, of course, easily available to the reader. Attention should, however, be drawn to the paper by Dr. W. Hume-Rothery, F.R.S., and Mr. G. V. Raynor, which is of fundamental importance to those interested in the application of X-ray methods to the determination of phase boundaries in metallurgical equilibrium diagrams. A spirit not only of rivalry but of distrust has undoubtedly arisen at times between the exponents of the newer X-ray methods and those investigators who have adhered to the older, well-established methods of thermal and microscopical analysis. The authors examine the relative merits of the two methods of approach in an extremely enlightening way, and the paper is not only of value to actual workers, but will enable the general reader to assess more critically the standard of accuracy attained in published researches. For the determination of liquidus and solidus curves the classical methods stand supreme. For the determination of solid solubility curves thermal analysis is of restricted value owing to the sluggishness of transformations in the solid state and must be supplemented by microscopical methods or more elaborate physical methods. Most solubility curves are now determined by the microscopical method, in which a sample of the alloy is annealed for a time sufficient to produce equilibrium, then quenched and examined to see how many phases it contained at the quenching temperature. Even if decomposition has occurred during quenching the regions which have undergone that decomposition can readily be distinguished as having been a homogeneous field at the higher temperature. In this respect the method has an advantage over the X-ray method, since any decomposition of the X-ray specimen on quenching makes the result unreliable. For example, the decomposition of the β-phase of copper-zinc or silver-zinc alloys during quenching, narrows the apparent range of the β field and makes its boundaries with adjacent fields appear to be vertical.

Most X-ray methods involve the use of filings. These must be derived from the alloy annealed in

lump form to attain equilibrium and quenched from this temperature, after which the filings are prepared and reannealed at the same temperature. In many polyphase alloys the filings for X-ray work are so fine that individual particles may consist of only one phase, and annealing of the filings alone cannot produce equilibrium. Just as in preparation for microscopical examination the annealing period must, of course, be sufficiently prolonged to ensure that equilibrium has been attained. It is moreover specially necessary in applying the X-ray method that the actual composition of the filings be determined. In one case mentioned by the authors filings prepared from a two-phase alloy were found after being sieved through a 250-mesh gauze to contain one phase only. Not only may there be a difference between the average composition of the filings and that of the lump, but there may be loss by volatilisation in some cases, or actual contamination by oxide, dust or other foreign material. The determination of the composition of the filings demands a special technique of analysis and the use of microchemical methods is necessary on account of the small quantities available.

For the high-temperature part of a diagram the authors state that the advantage may reasonably be said to lie with the classical methods. The successful application of X-ray methods to the determination of equilibrium at high temperatures requires the use of a high-temperature camera ; otherwise it is confined to cases where the solubility range is small or the boundaries nearly vertical. At lower temperatures the X-ray method is increasingly valuable provided that the specimens are given suitably long annealing treatments. Moreover, in diagrams involving super-lattice formation and other complex structural changes the X-ray method is the only one which can really deal with the facts, as etching methods will not in general distinguish between ordered and disordered modifications of the same structure. The commonly held idea that X-ray methods permit phase boundaries to be determined accurately by means of a few experiments on a very small number of alloys must, however, be discarded, and the final conclusion of Dr. Hume-Rothery's and Mr. Raynor's critical assessment of the methods is that nothing is gained, but much lost, if the X-ray investigator tries to determine an equilibrium diagram by X-ray methods alone.

The Freezing Point of Iron

ALTHOUGH many determinations of the freezing point of iron have been reported, there is still some uncertainty regarding the true value, because iron of high purity has not often been available for the measurements and because no determination has been carried out under entirely satisfactory conditions. Even after a relatively pure iron has been produced and its purity established, precautions must be taken to maintain that purity during the measurement of the freezing point because the metal is so readily contaminated by many crucible materials and gases during melting. Most of the values for the freezing point of iron were determined by thermo-couples. The purity of the standard metals (nickel or palladium), with which they were calibrated in the upper range of temperature, is sometimes uncertain, and the adjustment of the reported values to the same temperature scale offers difficulties.

Previous work has recently been reviewed and a new series of determinations reported by W. F. Roeser and H. T. Wensel.[1] These authors regard as the most trustworthy of all the values so far obtained that of Chipman and Marshall,[2] viz., 1535 deg. Cent. for iron which was probably saturated with hydrogen, and may have been slightly contaminated by silicon. Next in order come Burgess and Waltenberg's determinations[3] and reasons are given for preferring the method leading to the higher of their values, viz., 1533 deg., which on adjustment of the temperature scale becomes 1537 deg. Cent. The lower value, 1527 deg. Cent., reported by Jenkins and Gayler,[4] was attributed to absorption of light by iron vapour and failure to attain complete black-body conditions.

Roeser and Wensel, using the optical pyrometer of Fairchild and Hoover,[5] measured the freezing point of a sample of high purity (over 99·99 per cent.) iron prepared by Thompson and Cleaves[6] and melted in a beryllia crucible in an atmosphere of helium, which is considerably less soluble than hydrogen or nitrogen in iron and steel. The value obtained was 1539 ± 1 deg. Cent. When the iron was melted in hydrogen its freezing point was from 1 to 3 deg. lower, the depression probably varying on account of the uncertain amount of absorbed hydrogen present at the beginning of freezing. Measurement of the freezing point *in vacuo* gave the value 1536 deg. Cent., but the difference between 1539 and 1536 could be accounted for by the absorption of light by the iron vapour present.

The freezing point of Armco ingot iron in helium was 1534 ± 2 deg. Cent. A series of determinations was made on steels of different compositions and provides data for establishing the effects of various impurities and alloying elements on the freezing temperature of iron when several of the elements are

Depression of the Initial Freezing (Liquidus) Temperature of Iron per per cent. by Weight for each of the Impurities or alloying Elements Usually Found in Steels, and the Amounts of the Various Elements in the Materials Investigated.

Element.	Depression of freezing point per per cent. by weight, deg. Cent.	Range of elements in materials investigated (percentage by weight).
Hydrogen	1·300 computed	0 to ? (approx. 0·002)
Nitrogen	90 ,,	0 to 0·03
Oxygen	80 ,,	0 to 0·03
Carbon	Varies as follows : 65 at 0 per cent. 70 at 1 ,, 75 at 2 ,, 80 at 2·5 ,, 85 at 3 ,, 91 at 3·5 ,, 100 at 4 ,,	0 to 3·8
Phosphorus	30	0 to 0·7
Sulphur	25	0 to 0·08
Arsenic	14	0 to 0·5
Tin	10	0 to 0·03
Silicon	8	0 to 3
Manganese	5	0 to 1·5
Copper	5	0 to 0·3
Nickel	4	0 to 9
Molybdenum	2	0 to 0·3
Vanadium	2	0 to 1
Chromium	1·5	0 to 18
Aluminium	0	0 to 1
Tungsten	1	18 per cent. with 0·66 per cent. C

present at the same time. The results indicate that, in general, when a number of other elements are present in iron, the effect of any one is the same as it would be if the other elements were not present, and the total effect of all the elements is equal to the sum of the effects of the elements taken separately. Thus the initial freezing temperature of the steel can be calculated from the chemical composition by means of the data given in the accompanying table.

The method of computing the initial freezing temperatures of the steels from the chemical analysis and the lowering of the freezing point by the separate elements is entirely empirical and should be used with discretion. However, this method should prove useful in practice, as it seems to hold reasonably well for considerable ranges of composition.

REFERENCES

[1] U.S. National Bureau of Standards, *Journal of Research* April, 1941, 26, 273.

[2] *Jour. Amer. Chem. Soc.*, 1940, 62, 229.

[3] *Bulletin*, U.S. Bureau of Standards, 1914, 10, 79 (S 205).

[4] *Proc., Royal Society*, 1930, A 129, 91.

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[6] U.S. National Bureau of Standards, *Journal of Research*, 1939, 23, 163.

The Influence of Vanadium on the Scaling of Steel

IT appears from a review by H. Schrader on the influence of small alloy contents on the scaling and decarburisation of steel that little is known definitely about the effect of vanadium on oxidation phenomena. Tammann and Siebel from an examination of temper colours concluded that vanadium had a protective influence though Laissus could find no beneficial effect when the surface of the steel was enriched by vanadium to the extent of 4 per cent.[1] E. Scheil and K. Kiwit concluded that 4 per cent. of vanadium had only a slightly favourable effect on the scaling of soft iron and found that the layer between the metal and the scale became enriched with vanadium oxide.[2]

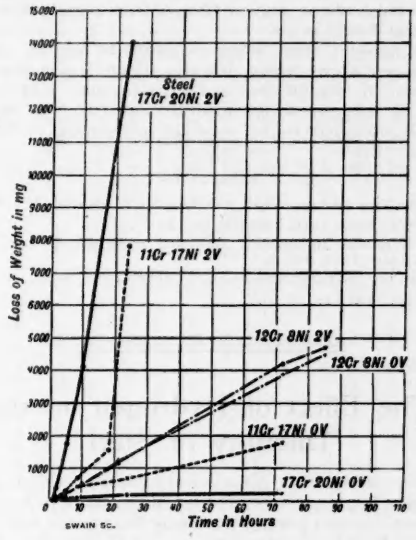
H. J. Schiffler[3] refers to the fact that against certain forms of attack scale resistance cannot be improved by small additions of molybdenum, vanadium, tungsten, copper, or cobalt. In several experiments a steel containing :—

	Per cent.
Carbon	0·44
Silicon	1·0
Manganese	0·9
Chromium	20·0
Nickel	14·4
Coba't	6·4
Vanadium	2·7

showed very small resistance to scaling in air at 800 deg., 900 deg., and 1000 deg. Cent., compared with a similar steel without vanadium. According to H. Cornelius and W. Bungardt,[4] scaling of a 10 per cent. aluminium steel in air at 1100 deg. Cent. is increased by a vanadium addition of 1 per cent.

These two authors (H. Cornelius and W. Bungardt) have now collected into a paper the results of their many interesting experiments on the scaling of alloy steels containing vanadium.[5] The addition of vanadium up to 4·7 per cent. to iron (carbon 0·03 per cent.) diminishes the rate of oxidation at 650 deg. Cent. It exerts a slight protective action against scaling in air up to 900 deg. Cent., but above this temperature it has no distinctive action. In steels of high resistance to scaling, *e.g.*, chromium or chromium-silicon steels, the addition of 0·5 to 2 per cent. of vanadium caused practically no change in behaviour, though with 2 per cent. vanadium scaling at the higher temperatures (*e.g.*, at 1100 deg. Cent.) was considerably increased.

The resistance to scaling of a chromium-nickel steel of high nickel content was not appreciably altered by the addition of 0·5 per cent. of vanadium, but a vanadium content of 2 per cent. in the same type of steel had a very unfavourable effect, which increased with increasing nickel content. The accompanying graph shows the relation between the loss of weight



Loss of Weight of Cr-Ni Steels, Without and With 2 per cent. of Vanadium, when Heated at 930 deg. Cent. in Air (Specimens 7 mm. diameter and 75 mm. long)

by scaling and the time of exposure of some chromium-nickel steels (with and without vanadium) to air at 930 deg. Cent. The steel with 12 per cent. of chromium and 8 per cent. of nickel shows a similar behaviour up to a period of 85 hours, both with 2 per cent. of vanadium and when vanadium-free. Up to a period of 18 hours the steel containing 11 per cent. of chromium and 17 per cent. of nickel with 2 per cent. of vanadium does not scale much more than the similar steel with no vanadium. With continued exposure, however, pronounced scaling occurs on the surface of the steel containing vanadium, though for much longer periods there is no sign of a similar effect on the vanadium-free steel.

The steel containing 17 per cent. of chromium and 20 per cent. of nickel showed a much greater difference due to the addition of vanadium. After 1 hour the scaling of the steel containing 2 per cent. of vanadium increased at a great rate. Thus the duration of the initial period of relatively slow scaling depended on the nickel content. With 8 per cent. of nickel it was not completed in 85 hours ; with 17 per cent. of nickel it was over in 18 hours ; and with about 20 per cent. of nickel in 1 hour. When this initial

period is exceeded there is a marked alteration in the nature of the scale. The smooth, compact, and strongly adhering scale first formed is replaced by a loose, friable scale with a rough surface. The cause of the change was not precisely stated. It was suggested that during the initial stage the surface of the specimen is preferentially losing chromium and vanadium by oxidation, and that the scale, not being impervious on account of the vanadium oxide present, permits rapid attack on the underlying surface now impoverished of its protective elements.

In a burnt coal gas atmosphere all the steels with 2 per cent. of vanadium were found to show a greater resistance to scaling than the vanadium-free steels, with the one exception of the 17 : 20 chromium nickel steel. Even in this steel the increased rate of scaling was only about one-twelfth of the corresponding increased rate in air.

It appears that, when exposure to air at temperatures above about 700 deg. Cent. is concerned, vanadium cannot be an advantageous addition, and it may be a detrimental constituent in alloy steels intended to be resistant to scaling at high temperatures.

REFERENCES

[1] See THE METALLURGIST, October, 1939, 1939–40, 12, 73.
[2] *Ibid.*, April, 1936, 1935–36, 10, 122.
[3] "Werkstoff-Handbuch," *Stahl und Eisen* (second edition), Dusseldörf, 1937, 0.91–2.
[4] *Archiv für das Eisenhüttenwesen*, 1939–40, 13, 539.
[5] *Ibid.*, 1941–42, 15, 107.

The Effect of Hydrogen on the Ductility of Steel

THE study of the influence of hydrogen on iron and steel is being actively pursued in Germany in several directions, and prominent among the present workers in the field are E. Houdremont and H. Schrader, who have recently published several papers on various aspects of the subject. Most of these papers have a bearing on flake formation, but attention is here directed to one of them which deals with the injury to the elongation and reduction of area of steel which, though not associated with actual formation of flakes, may result from annealing in an atmosphere of hydrogen.[1]

Previous work on hydrogen as a cause of low elongation and reduction of area of steel has already been dealt with in an earlier article[2] in which an outline was given of the work of F. Körber and J. Mehovar, who found that a short reheating at 200 deg. to 600 deg. Cent. produced a marked improvement in elongation and reduction of area of rail steel without any change in the yield point and tensile strength. The improvement was therefore not due to the softening treatment and was not connected in any way with the release of rolling or cooling stresses, but resulted, it was thought, from the elimination of certain microstructural stresses subsequently attributed to the presence of hydrogen. The article also contained a description of the more exhaustive study of the phenomenon by C. Drescher and R. Schäfer, who showed that in steels containing less than 0·4 per cent. of carbon the improvement in ductility could be effected by heating for twenty-four hours at 100 deg. Cent. Comparative tests before and after treatment for twenty-four hours at 100 deg. Cent. were made by H. Schottky on 0·2 to 0·3 per cent. carbon steel, melted under hydrogen, with the following results :—

	Untreated.	Heated for 24 h. at 100 deg. Cent.
Elongation, per cent.	10·9 to 13·5	18·9 to 21·8
Reduction of area, per cent.	12 to 23	36 to 50

Yield point and maximum load remained unchanged. In all this work the hydrogen, when special additions were required, was introduced into the liquid steel.

A very thorough investigation has now been made of the effect of annealing steel in a hydrogen atmosphere. The embrittlement of iron wire by heating in hydrogen has long been known,[3] and also the hydrogen embrittlement of electrodeposits and pickled sheet iron and its cure by heating at 100 deg. Cent., but Houdremont and Schrader have in this paper examined in a quantitative way the effect of hydrogen introduced by annealing at high temperatures.

They have investigated the effects of different times and temperatures of annealing and the influence of the composition of the gas atmosphere. The mechanical properties of carbon steels and of low and high

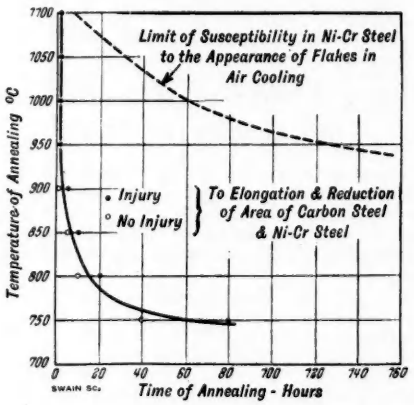

Limit of Susceptibility in Ni-Cr Steel to the Appearance of Flakes in Air Cooling
Temperature of Annealing °C
Injury
No Injury
To Elongation & Reduction of Area of Carbon Steel & Ni-Cr Steel
Time of Annealing - Hours
SWAIN Sc.

FIG. 1—*Effect of Hydrogen on a 60 mm. Square Bar in relation to Time and Temperature of Annealing in Hydrogen, followed by Air Cooling (Houdremont and Schrader)*

alloy nickel chromium steels annealed in this way, without or with subsequent heat treatment, have been determined in tests carried out at temperatures between +20 deg. and −80 deg. Cent.

An embrittlement which shows itself in fall of elongation and of reduction of area can be brought about by the absorption of hydrogen in the solid state, which results from annealing steels of even large cross section in hydrogen. In extreme cases this injury is associated with the formation of fine internal cracks which are visible on the fractured surface in the form of flakes.

The hydrogen content necessary to produce some damaging effect is, however, appreciably less than that required for flake formation. Moreover, a small moisture content in the atmosphere of the annealing furnce has a similar action to hydrogen though in a diminished degree.

Table I indicates some of the results and shows that twenty-four hours at 100 deg. Cent. is a very effective treatment in tending to restore the properties of the carbon steel and the nickel-chromium steel. The

extent of the injurious effect of annealing in hydrogen is dependent on the time and temperature of the annealing treatment as indicated in Fig. 1. A considerably higher temperature or more prolonged treatment than that which will damage the steel is required to confer susceptibility to flakes.

Work on parallel lines to that of Houdremont and Schrader has been carried out in America by C. A. Zapffe and C. E. Sims.[4] They produced specimens of steel with high hydrogen content by heating 0·505in. diameter tensile test bars for three hours in hydrogen at 1100 deg. Cent. and quenching in water. These hydrogen-rich steels were then reheated at temperatures from 100 deg. Cent. upwards and the high hydrogen pressure some fall in ductility was observed by Houdremont and Schrader. This behaviour is in agreement with the resistance offered by molten austenitic steels to the absorption of hydrogen, observed by W. Eilender, Yü Chih Chiu and F. Willems.[5] Some results on 18 : 8 chromium-nickel steel are contained in Table II. Whilst in carbon steel and relatively low alloy steel the hydrogen taken up is evolved during tempering at the low temperature of 100 deg. to 200 deg. Cent., higher tempering temperatures of 500 deg. to 600 deg. Cent. must be used to expel the hydrogen from austenitic steels.

In steels with high hydrogen content evolution of

TABLE I.—*Effect of Annealing in Hydrogen on the Tensile Properties of Two Steels. (Interval Between Air Cooling and Carrying Out of Test on the Air-cooled Specimens Seven Hours and on those Reheated at 100 Deg. Cent. Twenty-nine Hours)*

Heat treatment.	Steel with 0·36 per cent. C, 0·27 per cent. Si, and 0·52 per cent. Mn.					Steel with 0·36 per cent. C, 0·25 per cent. Si, 0·50 per cent. Mn, 1·24 per cent. Cr, and 4·39 per cent. Ni.				
	Brinell hardness.	Yield point, kg./mm.²	Maximum load, kg./mm.²	Elongation ($l=5\,d$), per cent.	Reduction of area, per cent.	Brinell hardness.	Yield point, kg./mm.²	Maximum load, kg./mm.²	Elongation ($l=5\,d$), per cent.	Reduction of area, per cent.
1 h. at 1100 deg. in H_2/air	197	39·4	68·1	15·1	41	555	167	185·7	0·5	17
1 h. at 1100 deg. in H_2/air/24 h. at 100 deg.	195	59·5	69·2	27·9	52	555	168	186·1	6·5	38
1 h. at 1050 deg. in H_2/air	197	39·2	68·6	15·4	44	555	167	186·2	2·5	17
1 h. at 1050 deg. in H_2/air/24 h. at 100 deg.	187	39·7	67·9	27·2	50	555	167	185·9	9·7	39
1 h. at 1000 deg. in H_2/air	197	38·4	67·2	18·7	44	555	169	186·4	4·7	21
1 h. at 1000 deg. in H_2/air/24 h. at 100 deg.	197	39·1	67·7	27·9	51	538	168	185·9	11·2	41
1 h. at 950 deg. in H_2/air	187	36·5	65·4	26·5	52	538	167	185·0	10·5	39
1 h. at 950 deg. in H_2/air/24 h. at 100 deg.	187	37·1	66·2	28·9	53	538	167	185·2	12·2	41
1 h. at 900 deg. in H_2/air	187	37·3	66·2	27·9	52	542	167	186·2	11·9	40
1 h. at 900 deg. in H_2/air/24 h. at 100 deg.	187	38·1	66·0	27·3	52	555	168	185·7	12·4	41
5 h. at 900 deg. in H_2/air	187	38·5	67·1	21·4	47	555	168	187·2	10·1	34
5 h. at 900 deg. in H_2/air/24 h. at 100 deg.	187	38·7	68·2	27·4	54	555	167	186·9	12·7	42
5 h. at 850 deg. in H_2/air	179	34·9	61·5	27·4	54	514	152	176·3	12·8	47
5 h. at 850 deg. in H_2/air/24 h. at 100 deg.	179	35·2	61·7	27·4	55	514	153	175·7	12·4	46
10 h. at 850 deg. in H_2/air	179	33·9	61·4	21·7	47	514	154	176·5	8·7	36
10 h. at 850 deg. in H_2/air/24 h. at 100 deg.	179	34·5	61·7	29·4	56	514	155	177·1	13·1	43
10 h. at 800 deg. in H_2/air	170	32·7	60·2	27·6	56	477	146	163·5	12·7	48
10 h. at 800 deg. in H_2/air/24 h. at 100 deg.	170	31·9	61·2	27·9	55	477	147	164·1	12·9	47
20 h. at 800 deg. in H_2/air	170	33·1	60·7	21·4	51	477	147	163·4	9·4	33
20 h. at 800 deg. in H_2/air/24 h. at 100 deg.	170	33·5	61·2	28·4	56	477	148	164·1	13·4	45
40 h. at 750 deg. in H_2/air	145	34·1	56·9	29·8	53	477	152	162·4	12·4	46
40 h. at 750 deg. in H_2/air/24 h. at 100 deg.	145	33·7	57·2	36·1	58	477	151	161·2	13·2	47
80 h. at 750 deg. in H_2/air	145	34·9	59·1	22·4	50	477	151	164·4	8·9	41
80 h. at 750 deg. in H_2/air/24 h. at 100 deg.	145	35·2	58·4	30·4	58	477	152	162·5	13·5	47

accompanying changes in ductility were compared with those occurring in another set of specimens similarly treated in the absence of hydrogen. The results were presented in a series of photographs of fractures showing how with longer times or higher temperatures of tempering the hydrogen tends to be completely eliminated. Times for the almost complete expulsion of hydrogen from these ½in. diameter bars and the full restoration of the ductility of the steel are given in a curve as follows :—Twenty-four hours at 100 deg., ten hours at 200 deg., five hours at 300 deg. and two and a-half hours at 400 deg. Cent.

Austenitic chromium-nickel steels (18 : 8) are not susceptible to the influence of annealing in hydrogen, although with long annealing times and specially the gas can be induced not only by heating to a raised temperature, but by cooling to a very low temperature. Examples of this effect are given in Table III. When steels are tested at temperatures below zero there is a tendency for elongation and reduction of area to fall as the temperature of test is lowered. In steels such as those referred to in Table III, however, cooling to low temperatures occasions an evolution of hydrogen and this first leads to an increase of elongation and reduction of area which then falls again with further lowering of the temperature of test. The notched bar impact value falls continuously. The maximum values of elongation and reduction of area obtained by lowering the temperature of testing of the steels of Table III occurred on

testing at —40 deg. Cent. and were as follows :—

	Carbon steel.		Ni-Cr steel.	
	+20 deg.	—40 deg.	+20 deg.	—40 deg.
Elongation, per cent. ...	17·2	27	7·6	17
Reduction of area, per cent.	31	48	12	42

The normal, constant or slightly falling values with diminishing temperature were observed in these steels after a preheating to 120 deg. Cent. for forty-eight hours, but twenty-four hours at 120 deg. Cent. for the nickel-chromium steel was insufficient and for the carbon steel barely sufficient to suppress the maximum which was evident when the steel had been heated for shorter times at this temperature (Fig. 2).

It is clear from Table III that the effect of very low temperatures is similar to that of holding at 120 deg. Cent., and it might therefore be inferred that, provided sufficient time were allowed, damage to elongation and reduction of area might be avoided by storage at atmospheric temperature. This, indeed, was the claim made by Körber and Mehovar, who found that, in specimens cut from a rail, storage for seven weeks was almost exactly equivalent in effect to one hour at 200 deg. Cent. These conclusions of Körber and Mehovar have been confirmed by C. Holthaus in a written discussion of Houdremont and Schrader's paper. Test pieces were taken from centre and outside of a 140 mm. square bar of a 0·32 per cent. carbon open-hearth steel immediately after hot

TABLE II.—*Embrittlement of 18 per cent. Chromium, 8 per cent. Nickel Austenitic Steel, by Annealing in Hydrogen and Partial Recovery by Annealing at 200 deg. to 600 deg. Cent.*

Time and temperature of annealing in hydrogen.	Gas pressure, kg./cm.²	Heat treatment.	Yield point, kg./mm.²	Maximum load, kg./mm.²	Elongation ($l=5\,d$), per cent.	Reduction of area, per cent.	Impact value,* mkg./cm.²
—	—	1050 deg. Cent. w.q.	28	63·7	65·6	70	—
1100 deg. Cent., 10 h. ...	1	Water quenched	21	58·8	62·2	70	—
,, 24 h. ...	1	,, ,, ...	23	59·4	64·4	62	—
,, 50 h. ...	1	,, ,, ...	21	55·7	57·5	56	—
—	—	1050 deg. Cent. w.q.	27	62·4	55·6	72	32·6
—	—	1050 Cent. w.q., re-heated for 100 h. at 600 deg. Cent., and furnace cooled	27	59·6	47·0	71	33·4
600 deg. Cent., 10 h. ...	300	Water quenched	30	63·5	50·0	70	32·1
,, 100 h. ...	,,	,, ,, ...	25	60·1	25·6	26	26·1
,, ,, ...	,,	W.q., then 8 h. at 200 deg. ...	35	60·7	20·0	19	23·8
,, ,, ...	,,	,, ,, 300 deg. ...	31	62·2	26·0	26	23·3
,, ,, ...	,,	,, ,, 400 deg. ...	32	64·5	34·8	28	22·8
,, ,, ...	,,	,, ,, 500 deg. ...	30	60·9	42·4	63	27·6
,, ,, ...	,,	,, ,, 600 deg. ...	28	60·1	48·4	70	30·2

* Specimen 55 by 10 by 10 mm., with 2 mm. diameter notch, 3 mm. deep.

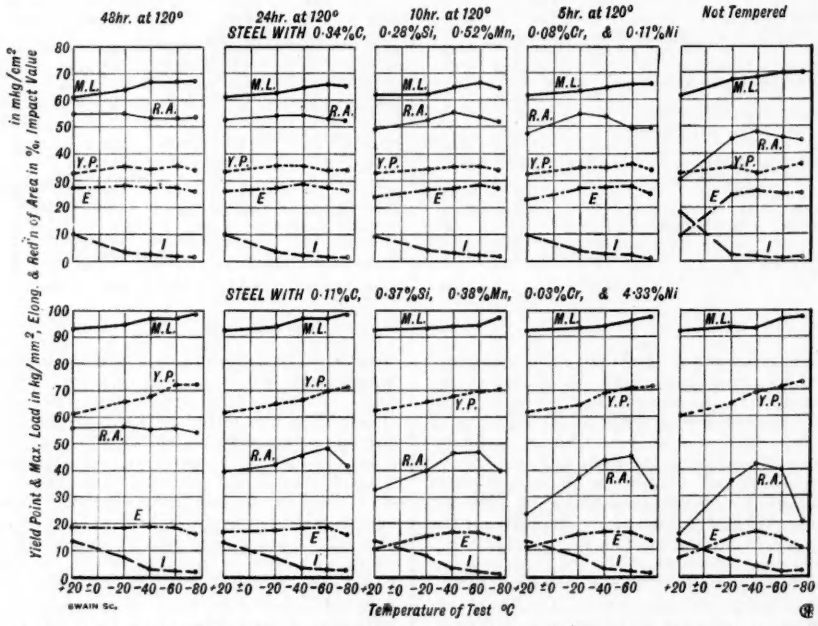

48hr. at 120°
24hr. at 120°
10hr. at 120°
5hr. at 120°
Not Tempered
STEEL WITH 0·34%C, 0·28%Si, 0·52%Mn, 0·08%Cr, & 0·11%Ni
STEEL WITH 0·11%C, 0·37%Si, 0·38%Mn, 0·03%Cr, & 4·33%Ni
M.L.
R.A.
Y.P.
E
I
Yield Point & Max. Load in kg/mm², Elong. & Red'n of Area in %, Impact Value in mkg/cm²
Temperature of Test °C
+20 ±0 -20 -40 -60 -80
GWAIN SC.

FIG. 2— *Effect of Annealing in Hydrogen for 5 hours at 1100 deg. Cent., and Subsequent Tempering on the Properties of Steel at Low Temperatures (Houdremont and Schrader)*

rolling from the ingot, and were tested without delay. Further test pieces were taken at intervals. Determinations of hydrogen content were made at each stage. The results are shown in Fig. 3. Ultimately the centre and outside gave the same tests, showing that in a non-segregated piping steel the difference in elongation and reduction of area at these positions is not due to depth of penetration of rolling stress or other similar influences, but may arise solely from difference in hydrogen content. One hour at 200 deg. Cent. achieved the same result as several weeks' storage at atmospheric temperature. The effect is, of course, only to be expected in steels which after casting (or high temperature annealing in hydrogen) have not received any treatment which would expel hydrogen.

TABLE III.—*Effect of Cooling in Liquid Air on the Tensile Properties at Room Temperature of Steels Annealed for 5 h. in Hydrogen at 1100 deg. Cent. and Air Cooled*

Composition of steel, per cent.					Further treatment.	Yield point, kg./mm.²	Maximum load, kg./mm.²	Elongation per cent. ($l = 5\,d$).	Reduction of area, per cent.	Impact value, mkg./cm.²
C.	Si.	Mn.	Cr.	Ni.						
0·34	0·28	0·52	0·08	0·11	None	33·4	62·3	17·2	31	6·1
					15 min. at −197 deg.	33·9	63·4	28·5	53	7·7
					48 h. at 120 deg.	32·9	62·7	26·7	51	9·1
0·11	0·37	0·38	1·03	4·33	None	60	91·3	7·6	12	12·3
					15 min. at −197 deg.	63	89·3	16·9	39	9·1
					38 h. at 120 deg.	62	91·3	19·4	54	13·8

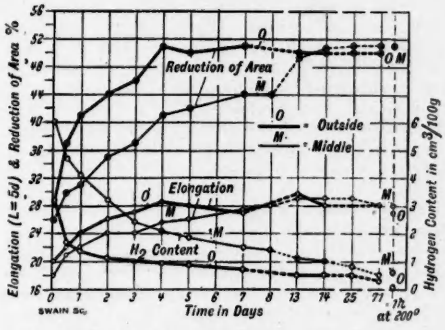


FIG. 3—*Effect of Storage at Room Temperature on the Hydrogen Content, the Elongation and the Reduction of Area of a 140 mm. Square Bar of 0·32 per cent. Carbon Acid Open-hearth Steel (Holthaus).*

REFERENCES

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[2] THE METALLURGIST, 1935–36, 10, 117.
[3] E. Heyn, *Stahl und Eisen*, 1900, 20, 837.
[4] *Metals Technology*, August, 1941, T.P., 1307.
[5] *Archiv für das Eisenhüttenwesen*, 1939–40, 13, 309.

The G.E.C. Heavy Alloy

THE *G.E.C. Journal* for August, 1941, contains the most complete account which has yet appeared of the heavy alloy made by sintering tungsten powder with copper and nickel, the first development of which and its use for radium containers were described by C. J. Smithells in 1937.

There are numerous engineering uses, which will be referred to later, for a metal or alloy of high density, but apart from the light alloys the ordinary structural materials possessing adequate strength have densities between 7·5 and 8·9. Lead (density 11·4) is weak mechanically, gold (19·3) and platinum (21·5) are excluded from use on account of their cost, and in this region of density tungsten (19·3) is the only element readily available. The production of large pieces of pure tungsten is not practicable, but tungsten powder can be sintered with a suitable bonding material into solid masses of alloy, having a density of 16·5–17·0, and a tensile strength equal to that of a good-quality steel.

As a result of extensive investigation, the composition selected as giving the best results is tungsten 90, nickel 7·5, and copper 2·5 per cent. The requisite quantities of tungsten, nickel, and copper powders, of a suitable degree of fineness, are thoroughly mixed together in the dry state. A small quantity of a suitable binder, such as a solution of wax in benzol, is then added, and the mixing continued until all the solvent has evaporated. The binder makes it possible to press coherent masses at much lower pressures than would otherwise be necessary, and for general purposes a pressure of from 5 to 10 tons per square inch is quite satisfactory.

The pressed pieces, which are strong enough to be handled, are supported on steel plates or refractory blocks, and slowly heated to a temperature of approximately 1000 deg. Cent. in a muffle furnace. A reducing atmosphere has to be maintained in the furnace, and it is necessary to carry out the initial stages of this firing slowly, if disruption of the pieces, due to too rapid evolution of the binder, is to be avoided. During this prefiring treatment, there is little tendency for the pressings to sinter and stick together, and consequently it does not matter if they are in contact with one another in the furnace. The second stage of the firing, namely, heating the pressings to a temperature at which a liquid phase is formed, is much more critical, and it is important that the pressings should not be in contact with one another during the high temperature firing. During this second firing, which must also be done in a reducing atmosphere, a linear shrinkage of up to 20 per cent. occurs on all dimensions, and this, of course, has to be allowed for in the designing of the dies. Heavy alloy prepared by this process is entirely free from porosity, and has the properties of alloys prepared by the more conventional methods of melting and casting.

In mixtures of tungsten and copper, the only effect of the sintering is that the molten copper wets the tungsten particles and cements them together. In alloys containing tungsten and nickel only, the tunsten particles are not completely wetted by the nickel, and a large amount of porosity is apparent. This is doubtless due to the melting point of the nickel phase being raised above the sintering temperature

by the solution of tungsten in nickel, so that eventually no liquid phase is present at the sintering temperature. Satisfactory alloys may, however, be obtained with tungsten and nickel only if a higher sintering temperature is employed. A very rapid change of density occurs in the 90 : 10 tungsten-nickel alloy as a result of raising the sintering temperature from 1450 deg. to 1500 deg. Cent.

In alloys containing both nickel and copper two factors are of importance—the ratio of nickel to copper and the total percentage of these metals present. The presence of too much liquid at the sintering temperature makes the body plastic and liable to lose its shape ; on the other hand, the sintering mechanism does not proceed satisfactorily if the nickel plus copper content is less than about 6 per cent. The total percentage is therefore fixed at 10 per cent. Copper lowers the melting point of the nickel, and thus ensures the presence of a liquid phase, which is able to penetrate between the tungsten grains, but at the same time it reduces the solubility of tungsten and so diminishes the cohesion between the tungsten particles and the nickel-copper phase, with detrimental results on the strength of the alloy. For maximum tensile strength, the nickel : copper ratio is 3 or 4 to 1, and for maximum density about 3 to 1. The composition now standardised for the production of Heavy Alloy is accordingly—tungsten 90, nickel, 7·5, and copper 2·5 per cent. Its more important physical properties are as follows :—

Tensile strength, tons per square inch ...	40
Yield point, tons per square inch	37
Elongation, per cent. on 1in.	4
Elastic modulus, lb. per square inch ...	32×10^6
Brinell hardness number	250–290
Specific gravity	16·3–17·0
Coefficient of expansion	$5{\cdot}6 \times 10^{-6}$
Thermal conductivity, C.G.S. units	0·25
Specific resistance, ohm. cm.$^{-3}$	$1{\cdot}16 \times 10^{-5}$

Various industrial applications of Heavy Alloy are briefly referred to. It was originally developed to meet the need for a high-density material in radium beam therapy. By the use of Heavy Alloy instead of lead, a very considerable reduction in the size of the container is made possible. Other applications of Heavy Alloy as a screening material include its use for screens in X-ray tubes, for cosmic ray absorption measurements, for the construction of surface applicators in radium treatment, and as a screening material in research work on radio-activity and radiographic examination of materials.

A great deal of Heavy Alloy is now used for the contacts of electrical circuit breakers. Its high melting point and consequent resistance to burning by the electric arc have made it a powerful aid in designing breakers of very high capacity. A comparatively thin layer of the alloy ($\frac{1}{32}$in. to $\frac{1}{4}$in. thick, according to circumstances) has been found to be sufficient to limit burning to a tolerable degree. The tips are pressed and sintered to the required shape, and then attached to the contact stems by electrical brazing or silver soldering. The stem and tip are then finished to size by grinding.

Another engineering use for Heavy Alloy is for balancing the moving parts of machines of all kinds. The fact that a rotating body made of Heavy Alloy is able to store twice as much energy as a piece of steel of the same size opens up further interesting possibilities. In considering engineering applications, it may be recalled that whereas tungsten is practically unmachinable, Heavy Alloy, although containing 90 per cent. of tungsten, behaves like many other constructional materials and can readily be machined.

In presenting such full information about the development of Heavy Alloy, the authors of the paper (Messrs. G. H. S. Price and S. V. Williams, of the G.E.C. Research Laboratories, and Mr. C. J. O. Garrard, of the Witton Engineering Works) have recorded a distinct metallurgical achievement which shows promise of interesting applications in the future.

Books and Publications

An Outline of Metallurgical Practice. By CARLE R. HAYWARD. Second edition, revised and enlarged. Medium 8vo, pp. xii+690. 1941. London : Chapman and Hall, Ltd. 38s.

THIS book is intended to give to readers an account in outline of the whole range of process metallurgy—the extraction and refining of metals—including a brief mention of mining and ore handling operations. It is clear that within the compass of a single volume it cannot be a detailed book of reference on the individual metals. Processes of historical or minor interest are omitted or referred to in only a few words. Long descriptions of plant and procedure find no place in the book. On the other hand, extensive use has been made of annotated photographs and drawings of industrial equipment mainly as used in American practice. This provides the reader with a much more vivid and realistic idea of the actual methods by which the operations described in the text are carried out than could be obtained from printed descriptions alone. Thus the book contains a surprisingly large amount of information in a form suitable for students or for engineers who require a general reference book on the subject. It also contains references to standard books on the individual metals.

Copper receives the largest share of attention, as there are so many operations in the metallurgy of copper which have a common interest to all metals. Next in order of amount of space occupied is the chapter on iron and steel. Beside the common metals, some elements which are rarely used in the metallic form, but in which interest has recently been aroused, come in for attention. Thus there are brief descriptions of the metallurgy of manganese, beryllium, vanadium, molybdenum and zirconium.

In an endeavour to make the book more comprehensive the author has included an account of the constitution and heat treatment of steel, an assessment of the functions of the alloying elements in the ferrous alloys and a chapter on non-ferrous alloys illustrated by equilibrium diagrams. The notes on the alloy steels are very brief and only a few of the simplest principles of heat treatment are described. The equilibrium diagrams are, as the author remarks, reproduced for the benefit of those who can understand them, and no explanation of their construction or meaning is given. The uninstructed student is therefore not likely to benefit very greatly from this part of the book, and, on the other hand, these sections are not sufficiently detailed to form a really useful work of reference. These features, however, though in themselves inadequate, may rightly be regarded as additional to the main theme. They supplement the discussion on the separate metals which forms the essential subject-matter of the book.

This new edition will be welcomed as a concise account of modern practice in the extraction of metals and a trustworthy guide to recent developments in process metallurgy, especially in America.